Jeongmin Ahn
School of Mechanical and Materials Engineering,
Washington State University,
Pullman, WA 99164

Paul D. Ronney
Aerospace and Mechanical Engineering,
University of Southern California,
Los Angeles, CA 90089

Zongping Shao
College of Chemistry and Chemical Engineering,
Nanjing University of Technology,
Nanjing, 210009 Jiangsu, PRC

Sossina M. Haile
Materials Science and Chemical Engineering,
California Institute of Technology,
Pasadena, CA 91125

A Thermally Self-Sustaining Miniature Solid Oxide Fuel Cell

A thermally self-sustaining miniature power generation device was developed utilizing a single-chamber solid oxide fuel cell (SOFC) placed in a controlled thermal environment provided by a spiral counterflow "Swiss roll" heat exchanger and combustor. With the single-chamber design, fuel/oxygen crossover due to cracking of seals via thermal cycling is irrelevant and coking on the anode is practically eliminated. Appropriate SOFC operating temperatures were maintained even at low Reynolds numbers (Re) via combustion of the fuel cell effluent at the center of the Swiss roll. Both propane and higher hydrocarbon fuels were examined. Extinction limits and thermal behavior of the integrated system were determined in equivalence ratio—Re parameter space and an optimal regime for SOFC operation were identified. SOFC power densities up to 420 mW/cm^2 were observed at low Re. These results suggest that single-chamber SOFCs integrated with heat-recirculating combustors may be a viable approach for small-scale power generation devices. [DOI: 10.1115/1.3081425]

1 Introduction

As is widely recognized, hydrocarbon fuels contain 100 times more energy per unit mass than lithium-ion batteries; thus, devices converting fuel to electricity at better than 1% efficiency represent improvements for portable electronic devices and other battery-powered equipment [1]. At small scales, however, heat and friction losses become increasingly significant, rendering devices based on existing macroscale designs such as internal combustion engines essentially impractical. Small-scale power generation devices using no moving parts may prove more feasible and offer overwhelming manufacturing advantages. One approach to achieving this goal is to utilize heat-recirculating or "excess enthalpy" burners, first studied 30 years ago [2,3], to drive thermoelectric, piezoelectric, or pyroelectric devices. In such burners, thermal energy is transferred from the combustion products to the reactants without mass transfer and thus without dilution of reactants. As a consequence, the total reactant enthalpy (sum of thermal and chemical enthalpy) is higher than that of the incoming cold reactants, enabling sustained combustion under conditions (lean mixtures, small heating value fuels, and large heat losses) that would extinguish without recirculation. This feature renders burner designs, such as the counter-current spiral "Swiss roll" heat exchanger and combustor, particularly attractive for small-scale power generation applications.

Solid oxide fuel cells (SOFCs) offer a convenient means of generating electric power from conventional fuels [4] and, given the absence of moving parts, may also be well suited to small-scale applications. Unlike proton exchange membrane (PEM) fuel cells, SOFCs can use hydrocarbon fuels directly and do not require fuel preprocessing to generate H_2 prior to utilization. Rather, H_2 and CO are generated in situ either by partial oxidation or, more typically, by steam reforming of the hydrocarbon fuel in the anode chamber of the fuel cell. The electrochemically active (reductant) species then reacts at the anode-electrolyte interface with oxide ions from the electrolyte, releasing electrons (e^-) to the external circuit. On the other side of the fuel cell, oxidant is fed to the cathode, where it supplies the oxide ions (O^{2-}) for the electrolyte by accepting electrons from the external circuit. The electrolyte conducts these ions between the electrodes, maintaining overall electrical charge balance. The flow of electrons in the external circuit provides useful power.

Conventional SOFCs typically operate at 800–1000°C, temperatures that are difficult to maintain at small scales due to significant heat losses. Furthermore, the seals that separate the anode and cathode chambers are subject to failure as a result of thermal shock during on/off cycling. These challenges have limited the applicability of SOFCs in small-scale portable power generation. To address these limitations, we have recently suggested the use of advanced SOFCs, which can operate both at reduced temperatures and in so-called "single-chamber" mode [5]. In contrast to conventional dual-chamber configurations, single-chamber fuel cells utilize a design in which the anode and cathode are exposed to the same premixed fuel-oxidizer stream [6,7]. The generation of voltage (and hence power) relies on the high selectivity of the anode and cathode catalysts. The single-chamber configuration greatly simplifies geometric constraints on SOFC systems and eliminates problems related to sealing failures. Furthermore, degradation due to carbon deposition or coking is mitigated as a result of the presence of oxygen in the fuel stream.

While advanced materials (ceria-based electrolyte and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode [8]) have lowered SOFC temperatures relative to conventional material sets, temperatures in excess of 400°C are still required for their operation. These high temperatures suggest that large heat losses and perhaps reaction quenching will occur in small-scale devices. Our previous work [9,10] has shown, however, that Swiss roll reactors can mitigate quenching at low Re. In light of those results, the objective of the present work is to assess the feasibility of utilizing a single-chamber SOFC in conjunction with a Swiss roll combustor for self-sustained thermal management at the low Reynolds numbers that would be encountered in a small-scale device. A single-chamber SOFC is placed immediately upstream of the center of a Swiss roll combustor, such that it is exposed to the unreacted hydrocarbon in the gas stream. Appropriate single-chamber SOFC operating temperatures are maintained via combustion of the fuel cell effluent at the center of the reactor.

2 Experimental Apparatus and Procedures

Experiments were performed by placing a single SOFC membrane electrode assembly (MEA), aligned parallel with the gas flow direction, in a three-turn, macroscale, spiral, counterflow Swiss roll reactor with a Pt strip catalyst at its center (Fig. 1). The

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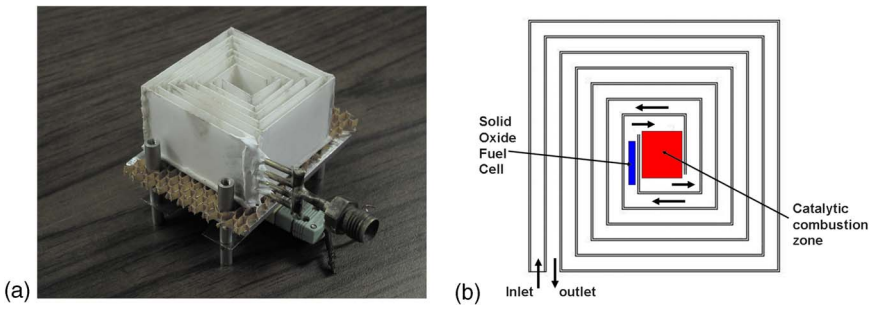

Fig. 1 (*a*) Ceramic Swiss roll reactor in an experimental stand with the top plate removed and (*b*) schematic of the experimental configuration showing the placement of fuel cell and the location of effluent combustion zone with Pt catalyst

reactor was constructed from sheets of boron nitride 0.6 mm in thickness, aligned and bonded using 904 zirconia Ultra Hi-Temp ceramic adhesive. The outside dimensions of the burner are approximately 5 cm wide×5 cm deep×3 cm tall. The gap-width for each inlet and exhaust channel is 3 mm. The top of the burner was sealed with approximately 3 mm of fibrous ceramic blanket, backed by 3 mm aluminum plates, and secured with Heat Shield ceramic adhesive. The fresh fuel-air mixture was provided through a manifold attached to the inlet of the Swiss roll. An electrically heated Kanthal wire wrapped around a ceramic post located at the center of the burner was used for ignition.

The fuel cell MEAs were constructed in an anode supported trilayer geometry using 15 mol % samaria doped ceria (SDC) as the electrolyte and Ni+SDC (NiO:SDC=60:40 weight ratio) as the anode. The cathode consisted of either $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)+SDC in a 70:30 weight ratio or $Sr_{0.5}Sm_{0.5}CoO_{3-\delta}$ (SSC)+SDC, also in a 70:30 weight ratio. A dual dry pressing method was used to obtain 13 mm diameter half-cells with ~20 μm thick electrolytes supported on ~700 μm thick anodes (~50% porous). Porous cathodes, 10–20 μm in thickness, were applied over an active area of approximately 0.7 cm^2 (Fig. 2). Full details of the fuel cell fabrication are presented elsewhere [11,12].

The reactor was instrumented with R-type thermocouples located at the center and in each inlet and exhaust turn (seven in total). Commercial mass flow controllers were used to regulate the flow rate of fuel (either propane or butane) and air through the reactor. LABVIEW data acquisition software was used to record the response of each thermocouple and to control the mass flow controllers. Tests were performed by placing the SOFC in the inlet turn closest to the center of the Swiss roll and by sustaining a propane-air oxidation reaction at the center of the reactor. Reported fuel cell temperatures are those recorded at the thermocouple just upstream of the fuel cell. Silver paste was used to connect gold wires to the electrodes at either side of the fuel cell. The wires were then insulated within the blanket and terminated outside the burner test stand. There, they were connected to a Keithley 2420 sourcemeter used for the measurement of polarization curves.

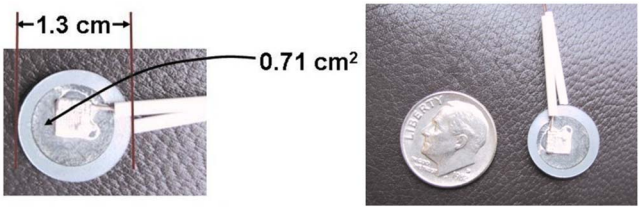

Fig. 2 Single-chamber solid oxide fuel cell

3 Results and Discussion

The lean and rich extinction limits and thermal behavior of the ceramic Swiss roll were thoroughly mapped prior to SOFC testing. Extinction limits were determined by starting from a steady burning state and by decreasing or increasing the fuel concentration with the igniter off. Self-sustained reactions with a bare platinum catalyst could be maintained within the Swiss roll at Reynolds numbers as low as 2. Furthermore, propane-air mixture compositions ranging from equivalence ratio of approximately 0.2 to 50 could be burned, and a range of temperatures from approximately 75°C to 1300°C could be sustained. Previous characterization of the fuel cells placed in an electrically heated tube furnace revealed that power generation in single-chamber mode required operating temperatures of 400–600°C and a fuel-rich environment with a fuel to oxygen ratio of ~1:2.25 for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)-based fuel cells [8] and ~1:3 for those based on $Sr_{0.5}Sm_{0.5}CoO_{3-\delta}$ (SSC) [11]. It was therefore determined that the ceramic Swiss roll could readily provide the conditions necessary for SOFC operation.

First recognizing that a temperature gradient exists across each channel of the Swiss roll, a SOFC (SSC-based) was tested in one case with the anode and in another case with the cathode facing the innermost side (hotter side) of the first inlet turn (from the center) of the Swiss roll (Fig. 1). Representative polarization curves obtained for each of the two configurations are presented in Fig. 3 with $C_3H_8:O_2=1:2$, Re=65, and T=480°C. It is immediately apparent that measurably higher output is obtained when the cathode is positioned facing the hotter wall of the first inlet turn. Similar behavior was observed over a range of conditions. The reasons for this behavior are not entirely obvious. Higher cathode

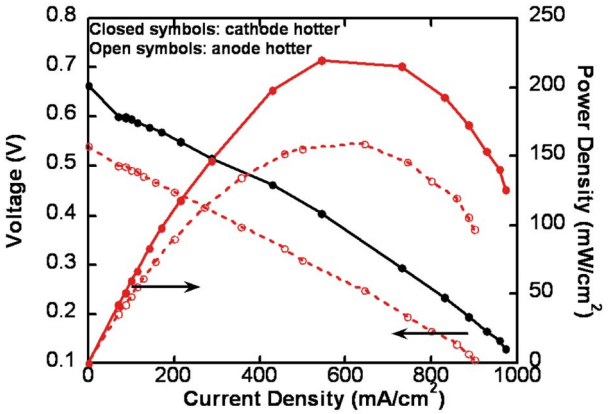

Fig. 3 Impact of fuel cell orientation relative to the hot zone in the Swiss roll reactor on electrical power output as measured for SSC-based fuel cell at T=480°C, $C_3H_8:O_2=1:2$, and Re=65

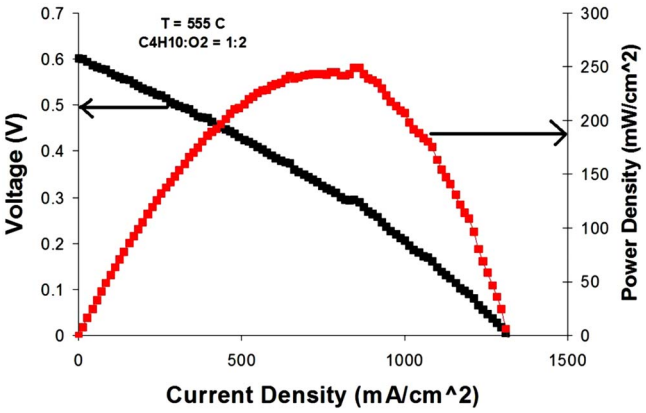

Fig. 4 Polarization and power density curves for SSC-based fuel cell at T=555°C, C_4H_{10}:O_2=1:2, and Re=80

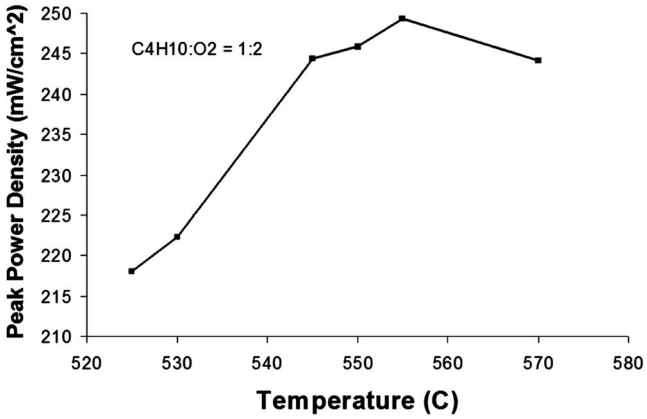

Fig. 5 Peak power density of SSC-based fuel cells as a function of temperature for C_4H_{10}:O_2=1:2 and Re=76 to Re=89

temperatures provide the benefit of higher electrocatalytic activity, but at very high temperatures, the drawback of direct fuel combustion appears [11]. Thus, one can envision an intermediate temperature at which cathode behavior is optimized. In contrast, both electrocatalytic activity and partial oxidation activity increase with increasing temperature of the anode, and thus monotonically improving performance might be envisioned for this component [11]. The results in Fig. 3, which contradict expectations based on activities of the individual component, point to the complexity of understanding the many coupled interactions in single-chamber fuel cells and the resulting subtle design trade-offs [13]. In any case, in recognition of the experimental observation, all subsequent results are presented for the configuration in which the cathode side of the fuel cell MEA faces the first inlet turn of the Swiss roll (i.e., is hotter). It is also noteworthy that the polarization behavior obtained for the SSC-based cell with the MEA appropriately oriented is remarkably similar to that obtained for an essentially identical cell operated in an electrically heated furnace under similar conditions. Specifically, at a furnace temperature of 525°C (anode temperature ~650°C) and a propane to oxygen ratio of 1:3, the open circuit voltage and peak power density were 0.75 V and 185 mW/cm^2, respectively, as compared with 0.68 V and 220 mW/cm^2 obtained here. The comparable electrical behavior confirms that the Swiss roll burner can indeed provide thermal and chemical environments suited to single-chamber SOFC power generation.

The SSC-based SOFCs were then tested with both propane and butane as fuel under a range of conditions. Butane has a somewhat higher energy density and lower vapor pressure than propane, which may be advantageous for applications, and results here focus on this fuel. The highest power output under butane (Fig. 4) was obtained for the following conditions: a Reynolds number of 80, a C_4H_{10}:O_2 ratio of 1:2, and a temperature of 555°C. As evident from a comparison to the data presented in Fig. 3, it is apparent that butane and propane react similarly in the miniature power generator, with butane leading to very slightly higher peak power output.

The behavior of peak power density as a function of temperature (with temperature increases achieved by increasing the gas flow rate, i.e., Re) for a fixed mixture composition (C_4H_{10}:O_2 =1:2) is shown in Fig. 5, and that as a function of mixture composition for fixed temperature (T=550°C) is shown in Fig. 6. In Fig. 5 the peak power density varies by only approximately 10% over the range of temperatures explored. The full polarization curves corresponding to these data (not presented) show that the current density at which peak power occurs does not change substantially with temperature. Given that the inherent electrochemical characteristics of this type of fuel cell are highly temperature dependent, the apparent insensitivity to temperature is likely a result of exothermic oxidation reactions occurring at the anode, which serve to maintain the fuel cell temperature at an approximately constant value across the range of nominal reactor temperatures. We have previously reported such behavior in the case of BSCF-based single-chamber fuel cells operated on propane [8], in which power output was insensitive to furnace temperature. In contrast, the dependence on mixture composition is relatively strong, decreasing almost monotonically as the mixture becomes less rich (i.e., becomes stoichiometric), from a maximum of about 255 mW/cm^2 at an optimal C_4H_{10}:O_2 ratio of ~1:2 to under 160 mW/cm^2 at a ratio of 1:2.8. Thus, the oxygen content corresponding precisely to partial oxidation appears to yield the highest power output. Behavior contrasts were observed when the fuel cells were operated in an electrically heated furnace. In that case, the optimal C_3H_8:O_2 ratio for maximum power output was ~1:3 [11], which is intermediate between the 1:1.5 corresponding to partial oxidation and the 1:5 corresponding to complete oxidation. As yet, it is unclear whether the difference in behavior can be attributed to differences in catalytic activity toward these two different fuels or to differences in the Swiss roll and furnace and environments.

The cathode material BSCF has a much greater electrochemical activity for oxygen electroreduction and much lower chemical activity for propane oxidation than SSC [8]. Thus, fuel cell power output from the BSCF-based fuel cells is much greater than that from the SSC-based fuel cells. A typical polarization curve obtained under propane is presented in Fig. 7 for the experimental conditions of C_3H_8:O_2=1:1.54, Re=85, and T=550°C. The peak power density was about 420 mW/cm^2, which, once again, cor-

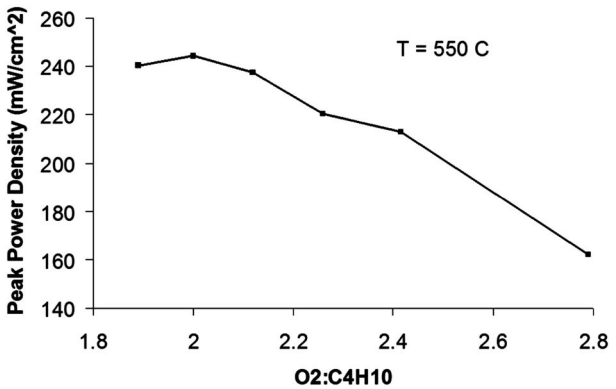

Fig. 6 Peak power density of SSC-based fuel cells as a function of reactant mixture composition at T=550°C and Re=74 to Re=92

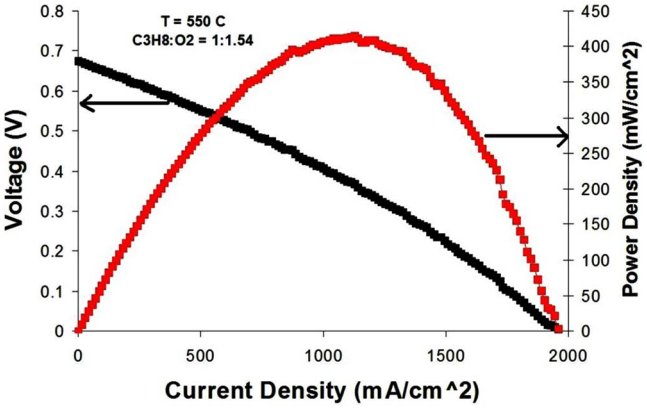

Fig. 7 Polarization and power density curves for BSCF-based fuel cell at T=550°C, C_3H_8:O_2=1:1.54, and Re=85

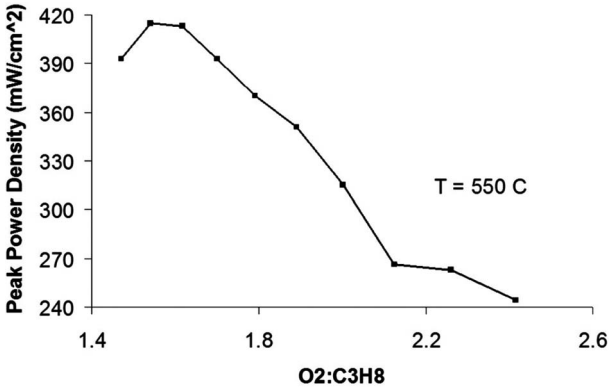

Fig. 8 Peak power density of BSCF-based fuel cells as a function of reactant mixture composition at T=550°C and Re=76 to Re=94

responds closely to the value obtained in an electrically heated furnace (~440 mW/cm^2). Figure 8 shows the behavior of peak power density as a function of mixture composition for a fixed temperature. As in the case of the SSC-based fuel cells operated on butane, the power output sharply decreased as the oxygen content in the reactant mixture was increased, falling to about 250 mW/cm^2 at a C_3H_8:O_2 ratio of 1:2.4. The result reveals that, once again, single-chamber fuel cell operation in an externally heated furnace temperature reaches maximum power output at oxygen to fuel ratios that are less lean than operation in a Swiss roll combustor. In this case, both sets of observations are made with propane as the fuel, and thus differences in the combustion environment must be responsible for the observed differences.

4 Conclusions

Experiments performed at low Reynolds numbers indicate that an integrated electric power generation system consisting of a single-chamber SOFC placed within a Swiss roll combustor is feasible. Here, the thermal environment is established by the reaction of the fuel cell effluent at the center of the reactor and does not require external heat inputs. Detailed mapping of both thermal and extinction limit behaviors of a ceramic Swiss roll in (Re, Φ) parameter space revealed that appropriate operating conditions for a single-chamber SOFC could be maintained via self-sustained reactions. The power outputs of two different types of SOFCs operated in a single-chamber mode were measured over a range of conditions using propane-air and butane-air mixtures. Reynolds numbers were varied from 40 to 100; C_4H_{10}:O_2 ratios were varied from 1:1.88 to 1:2.80; and C_3H_8:O_2 ratios were varied from 1:1.47 to 1:2.59. Under these conditions, measured peak power densities were comparable to those obtained from single-chamber fuel cells operated in an externally heated furnace. Specifically, for fuel cells incorporating $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) in the cathode, a maximum peak power density of about 420 mW/cm^2 was obtained for operation under propane, as compared with a maximum peak power density of about 440 mW/cm^2 recorded in a furnace. In addition, the power output was found to be apparently insensitive to reactor temperature, much as in the case of furnace operated single-chamber fuel cells. This has been explained in terms of the significant role of partial oxidation reactions at the fuel cell anode in controlling the actual fuel cell temperature. For reasons that are not entirely clear, superior performance was observed when the cathode side of the SOFC faced the hotter wall of the inlet channel. Moreover, power output was found to be highly dependent on reactant stream composition, with maximum power output in the Swiss roll reactor found to occur at compositions much richer than in the externally heated furnace. Overall, the results suggest that thermally self-sustained miniature solid oxide fuel cells incorporated into Swiss roll reactors may provide a solution for achieving high energy density in portable power applications.

Acknowledgment

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